BIDENTATE AMINE *N*-OXIDES AND PHOSPHINE OXIDES AS LIGANDS IN RHODIUM(I) CHEMISTRY

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Summary

Cationic rhodium(I) complexes of the general formula $[Rh(COD)L_2]ClO_4$ ($L_2 =$ bipyO_2, phenO, dpeO_2 and dpmO_2) are prepared from the solvated species $[Rh(COD)(Me_2CO)_x]^+$ and the appropriate ligand. Complexes of the type $[Rh_n(COD)_n(CNPyO)_n](ClO_4)_n$ (CNPyO = 4-cyano and 2-cyanopyridine *N*-oxide) are obtained similarly. Reaction of $[RhCl(COD)]_2$ with the potassium salt of 2-picolinic acid *N*-oxide leads to the neutral complex $Rh(COOPyO)(COD)$. The mononuclear rhodium diolefinic compounds react with carbon monoxide to give complexes of the type $[Rh(CO)_2L_2]ClO_4$ and $Rh(COOPyO)(CO)_2$, which on treatment with triphenylphosphine yield monocarbonyl derivatives.

The catalytic activities of the diolefin complexes and related derivatives in hydrogen-transfer catalytic reactions have been studied.

Introduction

Numerous cationic rhodium(I) diolefin complexes with nitrogen- or phosphorus-donor ligands have been reported [1], but only a few related compounds with oxygen-donor ligands have so far been described. Stable complexes are obtained with acetone [2,3], sulphoxides [2,4,5], monodentate pyridine *N*-oxides [6] and monodentate phosphine oxides [7].

Several cationic complexes of the general formula $[Rh(diolefin)L_2]ClO_4$, where L is a nitrogen-donor ligand [8–12], such as pyridine or an organic nitrile [11], are active catalysts in alkaline media for the transfer of hydrogen from isopropanol to several unsaturated substrates. On the other hand, recent reactivity studies [6] have shown that the pyridine *N*-oxide ligands have a coordination capacity between that of the pyridine and the nitrile ligands.

In this paper we report the synthesis of some rhodium(I) complexes with potentially bidentate ligands containing at least one oxide group. The behaviour of these compounds and related cationic rhodium complexes with amine *N*-oxides or phosphine oxides as catalysts in hydrogen-transfer reactions have been examined.

Results and discussion

Complexes with 2,2'-bipyridine N,N'-dioxide and 1,10-phenanthroline mono-N-oxide

Acetone solutions of [Rh(COD)(Me$_2$CO)$_x$]ClO$_4$ [13,14] react with 2,2'-bipyridine N,N'-dioxide (bipyO$_2$) [15] or 1,10-phenanthroline mono-N-oxide (phenO) [16] to give the square-planar cationic complexes [Rh(COD)(bipyO$_2$)]ClO$_4$ or [Rh(COD)-(phenO)]ClO$_4$. Bubbling carbon monoxide through dichloromethane solutions of these complexes leads to displacement of the coordinated cyclooctadiene and formation of [Rh(CO)$_2$(bipyO$_2$)]ClO$_4$ or [Rh(CO)$_2$(phenO)]ClO$_4$. These *cis*-di-carbonyl complexes react with stoichiometric amounts of triphenylphosphine to give [Rh(CO)(bipyO$_2$)(PPh$_3$)]ClO$_4$ (^{31}P NMR. δ = 49.7 ppm. (d. ^1J(Rh–P): 179 Hz)) and [Rh(CO)(phenO)(PPh$_3$)]ClO$_4$ (^{31}P NMR, δ = 45.1 ppm. (d, ^1J(Rh–P) 162 Hz)). These complexes can also be obtained by reaction of [RhCl(CO)(PPh$_3$)]$_2$ [17] with silver perchlorate and the appropriate ligand.

The complex [Rh(CO)(bipyO$_2$)(PPh$_3$)]ClO$_4$ reacts with stoichiometric amounts of triphenylphosphine to yield the compound [Rh(CO)(bipyO$_2$)(PPh$_3$)$_2$]ClO$_4$. Its IR spectrum shows ν(NO) bands characteristic of both coordinated and free N-oxide groups. suggesting that the bipyridine N,N'-dioxide acts as a monodentate ligand, as suggested for the corresponding silver complexes [18]. The ^{31}P NMR spectrum of the product shows a resonance at δ = 27.2 ppm. (d. ^1J(Rh–P) 127 Hz). This coupling constant suggests a *trans*-bisphosphine square-planar rhodium(I) structure [19].

Other routes to this complex are (i) reaction of RhCl(CO)(PPh$_3$)$_2$ [20] with silver perchlorate and bipyridine N,N'-dioxide and (ii) treatment of [Rh(CO)$_2$-(bipyO$_2$)]ClO$_4$ with triphenylphosphine in 1/2 molar ratio.

It is noteworthy that attempts to prepare the complex [Rh(CO)(phenO)-(PPh$_3$)$_2$]ClO$_4$ by the above routes were unsuccessful, [Rh(CO)(phenO)(PPh$_3$)]ClO$_4$ being the final product in all cases.

Complexes with 2-picolinic acid N-oxide

The dinuclear complex [RhCl(COD)]$_2$ [21] reacts with 2-picolinic acid N-oxide (H 2-COOPyO) [22] to give the neutral complex Rh(2-COOPyO)(COD). As expected, treatment of this complex with carbon monoxide followed by addition of triphenyl-phosphine gives the complexes Rh(2-COOPyO)(CO)$_2$, Rh(2-COOPyO)(CO)(PPh$_3$) and Rh(2-COOPyO)(CO)(PPh$_3$)$_2$. These compounds are non-electrolytes in acetone and their molecular weights in chloroform confirm the proposed formula.

The ^{31}P NMR spectrum of Rh(2-COOPyO)(CO)(PPh$_3$) shows two phosphorus resonances at δ 51.6 ppm. (d, ^1J(Rh–P) 178 Hz) and at δ 46.2 ppm. (d. ^1J(Rh–P) 178 Hz) probably corresponding to the two geometrical isomers, in ca. 55/45 ratio, where the triphenylphosphine is *trans* to an oxygen atom from either the carboxylic or the N-oxide group.

The IR spectrum of the complex Rh(2-COOPyO)(CO)(PPh$_3$)$_2$ shows that the NO group is not coordinated (ν(NO) 1276 and 1256 cm^{-1}) and that the carboxylate group acts as monodentate [23]. In addition, its ^{31}P NMR spectrum displays a signal at δ 29.0 ppm. (d, ^1J(Rh–P) 127 Hz) characteristic of *trans*-bisphosphine rhodium(I) complexes [19].

Complexes with 2- and 4-cyanopyridine N-oxide

Addition of stoichiometric amounts of either 2-cyanopyridine N-oxide (2-CNPyO)

[22] or 4-cyanopyridine N-oxide (4-CNPyO) [6] to an acetone solution of $[Rh(COD)(Me_2CO)_x]ClO_4$ gives complexes of the type $[Rh_n(COD)_n-(CNPyO)_n)](ClO_4)_n$, which separate from concentrated solutions as microcrystalline solids. In accord with this formulation, their ^1H NMR spectra show a molar ratio COD/CNPyO = 1/1. The IR spectra show a shift of both $\nu(CN)$ bands towards higher frequencies (ca. 40 cm^{-1}) and of $\nu(NO)$ towards lower frequencies (ca. 55 cm^{-1}) relative to the free ligands, indicating that both cyano and N-oxide groups are σ-bonded and hence bridge two rhodium atoms. Nevertheless, measurements of equivalent conductivities in nitromethane of the complexes $[Rh_n(COD)_n(2\text{-CNPyO})_n](ClO_4)_n$ and $[Rh_n(COD)_n(4\text{-CNPyO})_n](ClO_4)_n$ at different concentrations give plots of the Onsager equation ($\Lambda_0 - \Lambda_e = B\sqrt{c}$), for which the B values are 336 and 460, respectively, suggesting that dinuclear complexes may be present in solution [24].

Bubbling carbon monoxide through dichloromethane solutions of the complexes $[Rh_n(COD)_n(CNPyO)_n](ClO_4)_n$ gives cis-dicarbonylrhodium species [25,26], which are detected by IR spectroscopy. Addition of diethyl ether to these solutions does not lead to isolation of these complexes since the displaced cyclooctadiene returns to the coordination sphere of the rhodium atom with regeneration of the starting complexes. However, addition of equimolecular amounts of triphenylphosphine to solutions of the cis-dicarbonyl species leads to the isolation of diolefin-free solids. Their analytical, IR and ^{31}P NMR data suggest that they are mixtures of the complexes $[Rh_n(CO)_n(CNPyO)_n(PPh_3)_n](ClO_4)_n$ and $trans$-$[Rh(CO)(CNPyO)-(PPh_3)_2]ClO_4$.

Complexes with 1,2-bis(diphenylphosphine)ethane dioxide and bis(diphenylphosphine)-methane dioxide

Addition of stoichiometric amounts of either 1,2-bis(diphenylphosphine)ethane dioxide (dpeO$_2$) [27] or bis(diphenylphosphine)methane dioxide (dpmO$_2$) [28] to solutions of the solvated species $[Rh(COD)(Me_2CO)_x]ClO_4$ yields the cationic complexes $[Rh(COD)(dpeO_2)]ClO_4$ and $[Rh(COD)(dpmO_2)]ClO_4$. Bubbling of carbon monoxide through dichloromethane solutions of these complexes leads to displacement of the diolefin and formation of the cis-dicarbonyl complexes $[Rh(CO)_2-(dpeO_2)]ClO_4$ and $[Rh(CO)_2(dpmO_2)]ClO_4$, which are detected in solution by IR spectroscopy. Attempts to isolate the complexes from the solutions give the starting materials. However, these cis-dicarbonyl complexes can be prepared by reaction of the solvated species $[Rh(CO)_2(Me_2CO)_x]ClO_4$ with a stoichiometric amount of the appropriate ligand.

Addition of the stoichiometric amount of triphenylphosphine in molar ratio 1/1 to the above-mentioned cis-dicarbonyl complexes gives the compounds $[Rh(CO)(dpeO_2)(PPh_3)]ClO_4$ (XVI) and $[Rh(CO)(dpmO_2)(PPh_3)]ClO_4$ (XVII). The ^{31}P NMR spectra of both complexes show a resonance doublet corresponding to the phosphorus atom of triphenylphosphine at δ 50.0 ppm. (d, ^1J(Rh–P) 184 Hz) (complex XVI) and at δ 50.5 ppm. (d, ^1J(Rh–P) 186 Hz) (complex XVII), along with broad bands asignable to the phosphorus atoms of diphosphine dioxide ligands.

When triphenylphosphine is added in 2/1 molar ratio to the dicarbonyl complexes XI and XII the compounds $[Rh(CO)(dpeO_2)(PPh_3)_2]ClO_4$ (XX) and $[Rh(CO)(dpmO_2)(PPh_3)_2]ClO_4$ (XXI) are obtained. Their IR spectra display two $\nu(PO)$ bands corresponding to the free and coordinated ligand (see Table 1), along with one $\nu(CO)$ band. Thus, the complexes XX and XXI are assumed to be

TABLE 1

ANALYTICAL RESULTS, YIELDS, CONDUCTIVITIES, MOLECULAR WEIGHTS AND IR DATA FOR THE COMPLEXES PREPARED

Complex	Found (calcd.) (%)			Yield (%)	Λ_M^b (ohm^{-1}cm^{2}mol^{-1})	Mol.Wt.^{a,c}	IR data^d (cm^{-1})	
	C	H	N				ν(EO)^g	ν(CO)
I	[Rh(COD)(bipyO$_2$)]ClO$_4$	43.0 (43.4)	3.9 (4.0)	5.6 (5.6)	96	147	–	1203, 1186	–
II	[Rh(COD)(phenO)]ClO$_4$	47.8 (47.4)	3.9 (4.0)	5.6 (5.5)	95	143	–	1256, 1236	–
III	Rh(COOPyO)(COD)	48.1 (48.0)	4.6 (4.9)	4.2 (4.0)	78	–	304(349)	1271, 1229	–
IV	[Rh$_n$(COD)$_n$(2-CNPyO)$_n$](ClO$_4$)$_n$	38.4 (39.0)	3.7 (3.7)	6.7 (6.5)	84	89^e	–	1219	–
V	[Rh$_n$(COD)$_n$(4-CNPyO)$_n$](ClO$_4$)$_n$	39.3 (39.0)	3.8 (3.7)	6.7 (6.5)	98	95^e	–	1235	–
VI	[Rh(COD)(dpeO$_2$)]ClO$_4$	55.0 (55.1)	5.2 (4.9)	–	84	138	–	1142	–
VII	[Rh(COD)(dpmO$_2$)]ClO$_4$	55.1 (54.5)	5.3 (4.7)	–	86	137	–	1160	–
VIII	[Rh(CO)$_2$(bipyO$_2$)]ClO$_4^f$	32.7 (32.3)	1.8 (1.8)	6.1 (6.3)	87	144	–	1203, 1183	2094, 2020
IX	[Rh(CO)$_2$(phenO)]ClO$_4^f$	38.8 (37.0)	2.4 (1.8)	5.9 (6.2)	95	137	–	1253, 1234	2106, 2045

X	Rh(COOPyO)(CO)$_2$	32.6 (32.3)	1.5 (1.4)	4.7 (4.7)	40	–	338 (297)	1266, 1243	2102, 2030
XI	[Rh(CO)$_2$(dpeO$_2$)]ClO$_4$	48.2 (48.8)	3.7 (3.5)	–	65	143	–	1165	2096, 2036
XII	[Rh(CO)$_2$(dpmO$_2$)]ClO$_4$	48.1 (48.1)	3.3 (3.3)	–	60	136	–	1176	2084, 2016
XIII	[Rh(CO)(bipyO$_2$)(PPh$_3$)]ClO$_4$	50.8 (51.2)	3.7 (3.4)	4.1 (4.1)	66	122	–	1204, 1187	1984
XIV	[Rh(CO)(phenO)(PPh$_3$)]ClO$_4$	53.4 (54.0)	3.4 (3.4)	4.3 (4.1)	85	145	–	1255, 1236	1975
XV	Rh(COOPyO)(CO)(PPh$_3$)	56.9 (56.4)	3.8 (3.6)	2.7 (2.6)	58	–	572(531)	1270, 1233	1986
XVI	[Rh(CO)(dpeO$_2$)(PPh$_3$)]ClO$_4$	59.0 (58.6)	4.7 (4.3)	–	87	131	–	1140	1984
XVII	[Rh(CO)(dpmO$_2$)(PPh$_3$)]ClO$_4$	58.1 (58.1)	4.3 (4.1)	–	93	130	–	1160	1983
XVIII	[Rh(CO)(bipyO$_2$)(PPh$_3$)$_2$]ClO$_4$	59.0 (59.8)	4.1 (4.1)	2.7 (3.0)	81	126	–	{1213, 1186 / 1267, 1254}	2000
XIX	Rh(COOPyO)(CO)(PPh$_3$)$_2$	64.0 (65.0)	4.9 (4.3)	1.9 (1.8)	80	–	724(794)	1276, 1256	1969
XX	[Rh(CO)(dpeO$_2$)(PPh$_3$)$_2$]ClO$_4$	64.5 (63.8)	4.8 (4.6)	–	83	133	–	1190, 1153	1993
XXI	[Rh(CO)(dpmO$_2$)(PPh$_3$)$_2$]ClO$_4$	63.3 (63.6)	4.7 (4.5)	–	92	139	–	{1206, 1181 / 1152}	1977

a Calculated values are given in parentheses. b Acetone solutions. c Chloroform solutions. d Nujol mulls. e (Λ_e) Nitromethane solutions. f The compounds exploded violently in the microanalyzer. g E = N or P.

square-planar with only one coordinated PO group. The ^{31}P NMR spectra of these compounds show broad bands, suggesting fluxionality in solution.

General properties

The new complexes are obtained as air-stable yellow or orange microcrystalline solids. Their IR spectra show bands due to the oxygen-donor ligands. In particular, on coordination ν(NO) and ν(PO) are shifted towards lower wavenumbers relative to those of the free ligands [6,7]. The cationic complexes show the characteristic bands of the uncoordinated perchlorate group at ca. 1100 and 620 cm^{-1} and, as expected, are 1/1 electrolytes in acetone solution.

Catalytic activity

The diolefinic complexes are active catalyst precursors for hydrogen-transfer reactions from isopropanol to acetophenone and cyclohexene in the presence of potassium hydroxide (see Table 2).

Whilst the cationic amine *N*-oxide complexes (bipyO$_2$, phenO, 2-CNPyO, 4-

TABLE 2

REDUCTION OF ACETOPHENONE AND CYCLOHEXENE WITH RHODIUM(I) COMPLEXES CONTAINING OXYGEN-DONOR LIGANDS

Complexes	Conversion(%) after one hour	
	Acetophenone	Cyclohexene
[Rh(COD)(bipyO$_2$)]ClO$_4$	96 [a]	3
[Rh(COD)(phenO)]ClO$_4$	21	0
Rh(COOPyO)(COD)	11	28
[Rh$_n$(COD)$_n$(2-CNPyO)$_n$](ClO$_4$)$_n$	60	0
[Rh$_n$(COD)$_n$(4-CNPyO)$_n$](ClO$_4$)$_n$	17	2
[Rh(COD)(dpeO$_2$)]ClO$_4$	41	50
[Rh(COD)(dpmO$_2$)]ClO$_4$	19	24
[Rh(COD)(4-MeOPyO)$_2$]ClO$_4$	2	2
[Rh(COD)(4-MePyO)$_2$]ClO$_4$	3	14
[Rh(COD)(4-CNPyO)$_2$]ClO$_4$	56	1
[Rh(COD)(4-NO$_2$PyO)$_2$]ClO$_4$	0 [b]	53 [b,c]
[Rh(COD)((4-MeOC$_6$H$_4$)$_3$PO)$_2$]ClO$_4$	15	60
[Rh(COD)((4-MeC$_6$H$_4$)$_3$PO)$_2$]ClO$_4$	15	75
[Rh(COD)(Ph$_3$PO)$_2$]ClO$_4$	20	30
[Rh(COD)((4-ClC$_6$H$_4$)$_3$PO)$_2$]ClO$_4$	0	1
[Rh(COD)(Ph$_3$AsO)$_2$]ClO$_4$	2	0
[Rh(COD)(4-MeOPyO)(PPh$_3$)]ClO$_4$	57	27
[Rh(COD)(4-MePyO)(PPh$_3$)]ClO$_4$	13	7
[Rh(COD)(4-CNPyO)(PPh$_3$)]ClO$_4$	19	10
[Rh(COD)(4-NO$_2$PyO)(PPh$_3$)]ClO$_4$	91	24
[Rh(COD)((4-MeOC$_6$H$_4$)$_3$PO)(PPh$_3$)]ClO$_4$	95	23
[Rh(COD)((4-MeC$_6$H$_4$)$_3$PO)(PPh$_3$)]ClO$_4$	95 [d]	17
[Rh(COD)(Ph$_3$PO)(PPh$_3$)]ClO$_4$	95 [d]	10
[Rh(COD)((4-ClC$_6$H$_4$)$_3$PO)(PPh$_3$)]ClO$_4$	96 [d]	9
[Rh(COD)(Ph$_3$AsO)(PPh$_3$)]ClO$_4$	96 [d]	0

[a] 90% after 10 min. [b] Some decomposition to metallic rhodium was observed. [c] The observed 53% conversion is attributed to metallic rhodium [29]. [d] Ca. 95% is found after 10 min.

TABLE 3

COMPETITIVE REDUCTION REACTIONS WITH [Rh(COD)(L-L)]ClO$_4$ COMPLEXES

Complexes	Time (h)	Products (%)			
		Acetophenone	Cyclohexene	1-Phenylethanol	Cyclohexane
[Rh(COD)(bipyO$_2$)]ClO$_4$	0	50	50	0	0
	1	1	49.5	49	0.5
	2	1	47.5	49	2.5
[Rh(COD)(dpeO$_2$)]ClO$_4$	0	50	50	0	0
	1	43	31	7	19
	2	36	23	14	27

CNPyO) are more efficient catalysts for the reduction of acetophenone than for cyclohexene, the analogous complexes with phosphine oxides (dpeO$_2$, dpmO$_2$) and the neutral complex Rh(COOPyO)(COD) show the opposite behaviour. Table 3 shows the results of competitive reductions using the complexes [Rh(COD)-(bipyO$_2$)]ClO$_4$ and [Rh(COD)(dpeO$_2$)]ClO$_4$ as precursors, and reveals for the first complex a remarkable selectivity towards the selective hydrogenation of acetophenone.

Table 2 also lists the results obtained with other related complexes containing monodentate oxygen-donor ligands of the type pyridine N-oxide, triarylphosphine oxide and triphenylarsine oxide, the synthesis of which was described by us [6,7]. Cyclohexene is more efficiently reduced than acetophenone with catalyst precursors of the type [Rh(COD)L$_2$]$^+$, where L is triarylphosphine oxide. A similar behavior is observed with complexes containing phosphine dioxide ligands (dpeO, dpmO$_2$). On the other hand, a pronounced preference towards reduction of acetophenone is observed with precursors of the type [Rh(COD)L(PPh$_3$)]ClO$_4$, L being any of the oxygen-donor ligands.

Cationic complexes of the type [Rh(diolefin)L$_2$]$^+$ where L are nitrogen- or phosphorus-donor ligands, have been shown previously to be active catalysts for the transfer of hydrogen from isopropanol to some unsaturated substrates [8–12]. A relationship between the catalytic activity and ligand basicity was observed in some cases [11], but no clear-cut relationship is found for the the complexes listed in Table 2.

Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets or dichloromethane solutions in cells with NaCl windows. Conductivities were measured with a Philips PW 9501/01 conductimeter in ca. 5×10^{-4} M acetone or nitromethane solutions. ^{31}P{^{1}H}NMR spectra were recorded on a Varian FT-80A spectrometer using CDCl$_3$ or a mixture of CH$_2$Cl$_2$/CDCl$_3$ solutions. Chemical shifts are given in ppm relative to external 85% H$_3$PO$_4$, with a positive sign indicating a shift to lower field. ^{1}H NMR spectra were run in deuterated acetone. The molecular weights were measured in chloroform solution with a Hitachi-Perkin-Elmer mod. 115 osmometer.

Rhodium(I) complexes used as starting materials were prepared as described elsewhere [6,7]. The ligands 1,10-phenanthroline mono-N-oxide, 2,2'-bipyridine N,N'-dioxide, 2-picolinic acid N-oxide and cyanopyridine N-oxides were synthesised by literature methods [15,16,22]. The phosphine oxides were prepared by oxidizing the phosphines in acetone with an excess of dilute hydrogen peroxide [28] and recrystallized from acetone. The solvents were distilled before use. All the reactions were carried out at room temperature and atmospheric pressure with 0.1–0.2 mmol of the reagents.

Preparation of complexes of the type [Rh(COD)(L-L)]ClO$_4$(I, II, IV–VII)

A solution of [Rh(COD)(Me$_2$CO)$_x$]ClO$_4$ (obtained by treating [RhCl(COD)]$_2$ (0.049 g, 0.10 mmol) with AgClO$_4$ (0.041 g, 0.20 mmol) in 10 ml of acetone and removing the precipitated AgCl by filtration) was added to a suspension (complexes

I, II, VI, VII) or solution (complexes IV, V) of the corresponding ligand (0.20 mmol) in 10 ml of acetone. The solution was stirred for 30 min or until the ligand was completely dissolved. Concentration under reduced pressure to ca. 1 ml and slow addition of diethyl ether gave microcrystalline solids, which were filtered off, washed with diethyl ether and vacuum-dried.

Preparation of Rh(COOPyO)(COD) (III)

To a suspension of [RhCl(COD)]$_2$ (0.061 g, 0.12 mmol) and 2-picolinic acid N-oxide (0.034 g, 0.24 mmol) in 15 ml of methanol was added KOH (0.24 mmol) as a standardized solution in methanol. The resulting solution was stirred for 1 h. Vacuum concentration to dryness and extraction with dichloromethane gave a yellow solution. Concentration to ca. 1 ml and slow addition of diethyl ether gave a pale yellow precipitate which, was filtered off, washed with diethyl ether, and vacuum-dried.

Preparation of complexes of the type [Rh(CO)$_2$(L-L)]ClO$_4$

Complexes VIII and IX. Bubbling carbon monoxide through a solution of [Rh(COD)(bipyO$_2$)]ClO$_4$ or [Rh(COD)(phenO)]ClO$_4$ (0.10 mmol) in 15 ml of dichloromethane gave a precipitate of the corresponding cis-dicarbonyl complex. The precipitation was completed by addition of a small amount of diethyl ether. The microcrystalline solids were filtered off, washed with diethyl ether and air-dried.

Complexes XI and XII. To a solution of [RhCl(CO)$_2$]$_2$ (0.049 g, 0.13 mmol) and bis(diphenylphosphine) methane dioxide (0.106 g, 0.26 mmol) in 15 ml of dichloromethane was added (in the absence of light and under argon) a solution of AgClO$_4$ (0.053 g, 0.26 mmol) in 10 ml of acetone. The mixture was stirred for 1 h and the AgCl was filtered off. The yellow solution was evaporated to dryness under vacuum, to give a black solid, which was twice recrystallized from dichloromethane by slow addition of diethyl ether. The green-yellow precipitate was filtered off, washed with diethyl ether and vacuum-dried. The dpeO$_2$ compound (XI) was prepared similarly.

Complexes VIII and IX can also be obtained by this method.

Preparation of Rh(COOPyO)(CO)$_2$ (X)

Bubbling carbon monoxide for 10 min through a dichloromethane solution of Rh(COOPyO)(COD) (0.049 g, 0.14 mmol) led to an orange-coloured solution. Concentration to ca. 1 ml and slow addition of diethyl ether gave a yellow solid which was filtered off, washed with diethyl ether and vacuum-dried.

Preparation of complexes of the type [Rh(CO)(L-L)(PPh$_3$)]ClO$_4$ (XIII, XIV, XVI, XVII)

To a solution of [Rh(CO)$_2$(L-L)]ClO$_4$ (obtained by 10 min bubbling of carbon monoxide through a dichloromethane solution of complexes of the type [Rh(COD)(L-L)]ClO$_4$) was added the stoichiometric amount (1/1) of PPh$_3$ in dichloromethane. After 30 min stirring, the solution was concentrated under reduced pressure to ca. 1 ml. These complexes were crystallized by slow addition of diethyl ether. The resulting solids were filtered off, washed with diethyl ether and air-dried.

Preparation of complexes of the type [Rh(CO)(L-L)(PPh$_3$)$_2$]ClO$_4$ (XVIII, XX, XXI)

Addition of a stoichiometric amount of PPh$_3$ (2/1) to a dichloromethane solution

of complexes [Rh(CO)$_2$(L-L)]ClO$_4$ (prepared as described above) gave yellow solutions. The work-up was carried out as for the mono-triphenylphosphine complexes.

Preparation of Rh(COOPyO)(CO)(PPh$_3$) and Rh(COOPyO)(CO)(PPh$_3$)$_2$ (XV and XIX)

These complexes were prepared as described above by reacting complex X with PPh$_3$ in 1/1 or 1/2 ratio.

Catalytic activity

The transfer hydrogenation reactions were carried out under argon in refluxing isopropanol with magnetic stirring. The equipment consisted of a 50 ml round bottom flask, fitted with a condenser and provided with a serum cap. The catalysts were prepared by adding 0.1 mmol of KOH in 1 ml of isopropanol to an isopropanol solution (8 ml) of the corresponding rhodium(I) complex (0.02 mmol). The resulting solution was refluxed for 1 h and 2 mmol of the substrate in 1 ml of isopropanol was injected. Samples ca. 0.1 ml were taken at required times and were presently analyzed with a Perkin-Elmer 3920 B chromatograph connected to a Perkin-Elmer M-2 calculation integrator.

Acknowledgement

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